# Effect of hydrostatic pressure on the excitonic spectra of CsI crystals

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The excitonic reflection spectra of CsI crystals under pressures up to 12.5 kbar and $T = 80$ K are measured. The hydrostatic deformation potential for the first three excitonic transitions is determined. The interaction of excitonic levels is found to satisfy the Wigner-Neumann nonintersection rule.

In recent years, there has been a new and interesting development in the physics of excitons in ionic crystals involving the effects of self-localization of excitons.[1,2] The self-localization is due to the interaction of excitons with acoustic phonons and its nature depends strongly on the characteristics of the band structure of the crystal and the magnitudes of the deformation potentials.[1,3,4] For this reason, an accurate determination of the deformation potentials, just as the fundamental possibility of changing the position of the actual extrema of the bands by external pressure, are of great importance in the study of self-localization processes.

In this connection, crystals of cesium iodide CsI($O_h^1$) are of special interest. Calculations[5,6] show that the lower edge of the conduction band of CsI is formed by $s$-type

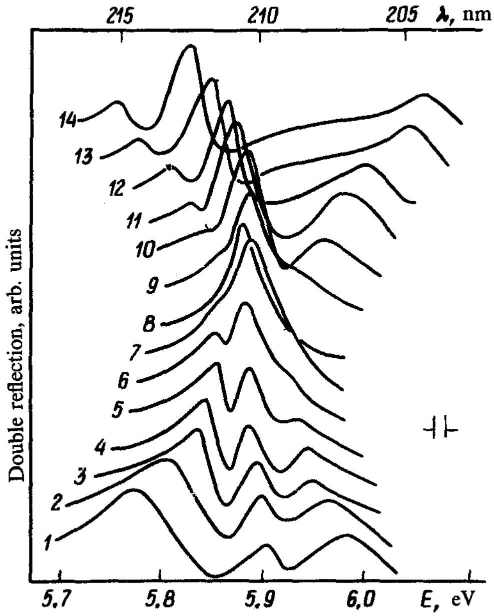

FIG. 1. Double reflection spectra of CsI crystals at 80 K at the following pressures: 1—1 atm; 2—0.9; 3—1.8; 4—2.4; 5—3.4; 6—4.0; 7—5.0; 8—5.5; 9—6.0; 10—7.1; 11—7.8; 12—9.7; 13—10.6; 14—12.3 kbar.

states ($\Gamma_6^+$ representation). The *d*-type states ($\Gamma_8^+$) are situated ~0.1 eV above them. The first three excitonic transitions studied by us are related to the interband transitions $\Gamma_8^- \to \Gamma_6^+$ and $\Gamma_8^- \to \Gamma_8^+$.1) These transitions correspond to bands in the reflection spectrum (Fig. 1, curve 1) at $5.76 \pm 0.02$, $5.90 \pm 0.01$, and $5.97 \pm 0.02$ eV (taking into account the spread for different crystals). The first and third peaks correspond to singlet states, and the peak at 5.9 eV corresponds to the triplet state. The transition to the triplet state becomes optically allowed because of the mixing with singlet states due to the deviation from analyticity of the *d* band at the $\Gamma$ point.[5]

The CsI and CsI–Tl (0.5%) crystals were compressed with the help of a high gas pressure setup,[7] consisting of a 15-kbar helium compressor, an optical chamber with leucosapphire windows, and a nitrogen cryostat. The spectra of double reflection of light at an angle of 10° from two polished crystals positioned in a special holder were measured. A deuterium lamp DL(D), a diffraction monochromator (dispersion ~13 Å/mm), and a PM-142 photomultiplier with a photon counting system were used.

Figure 1 shows the reflection spectra of CsI at 80 K, measured at different pressures in the range 0–12.5 kbar, and the points in Fig. 2 show the pressure dependence of the energy of excitonic transitions. This dependence can be separated into three regions: $P = 0$–$3.5$ kbar, the region of convergence of excitonic bands; $P = 3.5$–$6.0$ kbar, the region of strong interaction of excitons; and $P > 6.0$ kbar, the region of divergence of the bands and the appearance of additional structure. It should be noted that according to Fig. 2, the pressure coefficients for excitonic transitions, which are associated with the *s*-band (the lines *S* and *S'*) and *d*-band conductivity (the lines *T*, *T'*

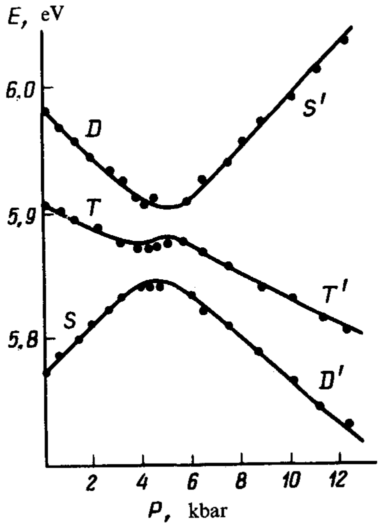

FIG. 2. Experimental (points) and computed dependences of the energy of excitonic transitions in CsI on the pressure.

and $D$, $D'$) have opposite signs. In addition to the displacement of the bands, there is a significant change in their intensities (Fig. 1): As the pressure is raised to 5.5 kbar, the intensity of the "forbidden" $T$ band increases substantially, and then again decreases. At $P \approx 5.5$ kbar, only this one band is observed in the spectrum.

The behavior of the three excitonic bands can be explained in terms of a model which takes into account the interaction (mixing) of excitonic levels, in addition to the pressure-induced displacements of these levels. If the excitonic levels are enumerated in order of increasing energies, then the Hamiltonian of the system in the exciton representation can be written in the form

$$H_{mn} = (E_{0n} + \alpha_n P)\delta_{mn} + \beta_{mn}(1-\delta_{mn})P \qquad (m, n = 1, 2, 3),$$

where $E_{0n}$ are the energies of the exciton levels at zero pressure, $\alpha_n = dE_n/dP = -\kappa \mathscr{E}_d^{(n)}$ are the pressure coefficients [$\kappa$ is the compressibility and $\mathscr{E}_d^{(n)}$ is the hydrostatic (completely symmetrical) deformation potential], and $\beta_{mn}$ are the coefficients of pressure-induced mixing of the levels (mixing at $P=0$ is assumed to be included in $E_{0n}$). The coefficients $a_n$ and $\beta_{mn}$ were determined from the conditions of best agreement with experiment and for $S$, $T$, and $D$ bands are respectively $\alpha_1 = +21$, $\alpha_2 = -8.5$, $\alpha_3 = -19$, $\beta_{12} = 4.6$, $\beta_{13} = 0$, and $\beta_{23} = 3.3$ meV/kbar. The maximum error for $\alpha_n$ is $\pm 2$ meV/kbar. The positions of the excitonic levels calculated from these parameters are represented in Fig. 2 by the solid curves. The interaction of the levels is realized via the triplet state. After the closest approach at $P \approx 5.5$ kbar, the $S'$ level moves away from the two other levels and acquires the properties of the $S$ level. The states $T$ and $D$ remain mixed at all pressures.

We note that the sign of the long-wavelength pressure-induced shift of the $D'$ band at $P > 6$ kbar agrees with the sign of the shift of the absorption edge of CsI at superhigh pressures up to 0.6 Mbar.[8,9]

Using the value of $\kappa$ for CsI at 77 K,[10] we obtain $\mathscr{E}_d^{(1)} = -2.9 \pm 0.3$, $\mathscr{E}_d^{(2)} = +1.2 \pm 0.2$, and $\mathscr{E}_d^{(3)} = +2.7 \pm 0.3$ eV. For $\Gamma$ excitons, which are linked with the $s$-band conduction in KI and RbI, we have obtained the approximate values $\mathscr{E}_d$ $-2.3$ and $-2.7$ eV, respectively. The values of $\mathscr{E}_d^{(1)}$ and $\mathscr{E}_d^{(3)}$ for CsI are close to the computed deformation potentials for the interband transitions $\Gamma_8^- \to \Gamma_6^+$ ($-2.36$ eV) and $\Gamma_8^- \to \Gamma_8^+$ (2.74 eV).[6] This suggests that the displacement of the excitonic levels primarily follows the displacement of the band edges. It follows that the $s(\Gamma_6^+)$ and $d(\Gamma_8^+)$ conduction bands intersect at pressures near ~5.5 kbar.[2] On the other hand, since the excitonic states have the same symmetry ($\Gamma_{15}$), the exciton levels do not intersect, consistent with the well-known Wigner-Neumann rule that forbids crossing of levels of identical symmetry. To the best of our knowledge, this effect for excitons under hydrostatic pressure has been observed for the first time.

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[1] The $\Gamma_{15}$ representation, which describes the symmetry of dipole-allowed excitons, enters twice into the product $\Gamma_8^- \times \Gamma_8^+ \times \Gamma_1$, where $\Gamma_1$ is the symmetry of the envelope of the exciton wave function.

[2] On the basis of an investigation of CsI at pressures up to 3.4 kbar, it was previously assumed in Ref. 11 that these bands intersect at ~7 kbar. In this study the doublet structure, 5.90 and 5.97 eV, was not resolved, and $\mathscr{E}_d$ for the two observed bands, 5.78 and 6.01 eV, was estimated to be $-2.1$ and 2.1 eV, respectively.

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